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EFFECT OF FELDSPAR CONCENTRATE COMPOSITION ON STRUCTURE AND PROPERTIES OF CERAMIC MIXTURES

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Feldspar concentrates produced from concentrated rocks of Karelia are investigated as components of hard porcelain mixtures. The effect of feldspar concentrates having different ratios of potassium and sodium oxides, the mineralogical composition, and the structural specifics on the structure and properties of porcelain mixtures is studied. It is established that the grain structure and the ratio of quartz and feldspar in the concentrate have a great significance for the formation of the vitreous phase in the fired sample.

Feldspar concentrate is used in ceramics mixtures as a flux. Compared to other components, the feldspar concentrate has a low melting point and in firing forms a vitreous phase contributing to the sintering of the components, which imparts strength, water tightness, and whiteness to the product. The sintering interval depends on the content of alkaline and alkaline-earth oxides in the feldspars [1].

The present study considers the effect of feldspar concentrates having different ratios of potassium and sodium oxides and different mineralogic compositions, and the structural specifics on the structure and properties of hard porcelain mixtures.

The concentrates introduced in hard porcelain mixtures were obtained from rocks of different genetic types from Karelia: the Chupinskoe deposit pegmatites, acid rocks of volcanic origin, i.e., hälleflinta from the Kostomukshskoe deposit and quartz porphyry from Roza-Lampi, and alkaline sienites from the Yelet'ozerskoe deposit. The chemical compositions of the concentrates are given in Table 1.

The pegmatite concentrate was concentrated using a method which included flotation and electromagnetic separation. The resulting feldspar concentrates consist of (here and elsewhere mass content in percent is indicated): microcline — 37.6 (sample No. 1), 10.4 (sample No. 2), 4.7 (sample No. 3); albite — 34.1 (sample No. 1), 51.4 (sample No. 2), 51.0 (sample No. 3); anorthite — 5.4 (sample No. 1), 11.9 (sample No. 2), 8.6 (sample No. 3); quartz — 22.8 (sample No. 1), 26.3 (sample No. 2), 35.0 (sample No. 3). The iron oxide content is below 0.2%. The ratio of K_2O : Na_2O varies from 0.09 to 2.03%, and the sum of the alkaline oxides varies from 7.92 to 11.6%.

The nepheline-feldspar concentrate based on alkaline sienites was concentrated by a simple technological scheme consisting of electromagnetic separation. The concentrate contains 65% microcline, 31.5% albine and nepheline, and 0.2 iron oxides. The sum of potassium and sodium oxides is 14.26%, and the potassium modulus is equal to 1. The concentrated material has a coarseness of 80% and belongs to class 0.1 mm. The composition of the rocks is constant. The quantity of nepheline varies from 1.5 to 2.5%.

The quartz-feldspar concentrate based on sodium hälleflinta was produced by wet magnetic separation using a polygradient separator, including a separator made by Sallo (Sweden). It was found that a concentrate with the minimal

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TABLE 1

Concentrate	Mass content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	$K_2O + Na_2O$	$K_2O : Na_2O$
Pegmatite:									
Pl-1	72.38	15.03	0.08	1.15	0.20	7.48	3.68	11.16	2.03
Pl-2	73.31	15.62	0.16	2.69	0.30	1.92	6.00	7.92	0.32
Pl-3	69.86	19.04	0.05	2.16	0.07	0.80	8.02	8.82	0.09
Hälleflinta	74.76	15.75	0.07	3.00	Traces	0.18	6.24	6.65	0.05
Quartz porphyry	79.65	11.76	0.19	0.20	0.20	7.50	0.50	8.00	15.00
Nepheline-sienite	64.17	20.50	0.20	0.87	Traces	6.73	7.53	14.26	0.90

(0.07%) content of iron oxide can be produced by grinding the initial material to 98%, class 0.074 mm. The concentrate contains 6.65% potassium and sodium oxides, and the potassium modulus is equal to 0.2.

Hälleflinta, unlike pegmatites, by nature has a consistent composition. Its main bulk is decrystallized glass containing 68.5% feldspar and 24.5% quartz.

A typical feature of the hälleflinta concentrate is its fine-grained structure in which the finely disperse quartz is in close agglomeration with extremely fine grains of albite in a ratio close to the eutectic. Previous investigations demonstrated that the closeness of the composition to the eutectic decreases the temperature of the beginning of melting, and the finely disperse quartz is more easily dissolved in the vitreous phase, thus increasing its viscosity [2].

The quartz porphyry from Roza-Lampi by its structure and mineral composition is similar to hälleflinta and is concentrated by a similar technologic scheme using electromagnetic separation. It contains (%): 45.5 quartz, 40.9 potassium feldspar, 5.0 plagioclase, 5.8 sericite, 0.5 biotite. A typical peculiarity of quartz porphyry is its insignificant content of alkaline-earth oxides, a high content of potassium oxide, and a low content of sodium oxide (0.5%). The quartz-feldspar concentrate made of quartz porphyry is represented by iron oxides (0.19%) and potassium and sodium oxides (8.0%), and the potassium modulus is equal to 15.

To study the effect of the chemical and mineralogical composition of feldspar concentrate on the structure and properties of porcelain, hard porcelain mixtures were prepared. The batch compositions of the experimental mixtures are shown in Table 2. All mixtures were prepared by wet grinding in a ball mill. The coarseness of grinding was determined by the residue 0.9 – 1.2% on a No. 0056 sieve. The moisture of the mixtures in molding was 23.5%. The dried samples 50 × 50 × 8 mm were fired at a temperature of 950 – 1380°C with an interval of 50°C.

The structure of the experimental porcelain mixtures was studied using x-ray, electron microscope, and petrographic methods of analysis. The phase composition was determined by x-ray phase analysis.

The phase composition of the samples was analyzed on a DRON-3.0 x-ray unit with CuK_λ and FeK_λ radiation within the range of S between 0.17 and 6.5 Å

$$S = 4\pi \sin\theta/\lambda,$$

where θ is the scattering angle and λ is the wavelength of the radiation used.

The distribution of diffracted radiation intensities was registered both on a diagram tape of the recording device and in the automatic mode by scanning within the specified range of S with step $S = 0.05$ Å and data output on a computer connected to the x-ray device.

According to the x-ray phase analysis data, the introduction of feldspar concentrates with different contents of microcline, albite, anorthite, and quartz into the hard porcelain mixtures does not produce significant changes in the phase composition. All mixtures have the amorphous-crystalline structure. The x-ray patterns show an increase in the vitreous phase content in the mixtures with plagioclase pegmatite (2, 3), with hälleflinta (4), and with nepheline sienite (6), which is probably related to the increased content of albite and anorthite in the concentrates whose $K_2O : Na_2O$ ratio is below 1.

The crystal phases are represented by mullite $Al_6Si_2O_{13}$ (0.212, 0.229, 0.339 nm) and low-temperature α-quartz (0.228, 0.245, 0.334 nm). The strongest reflections are observed in mixture 5 with the quartz porphyry concentrate. This is indicated by the increase in the mullite content, since the mullite band becomes visible (0.538 nm) and the peaks of the other bands become higher. The density of the specified crystalline phases is 3.18 g/cm^3 (mullite) and 2.66 g/cm^3 (α-quartz). However, the experimentally measured pycnometric density of the samples is within the interval of 1.68 – 2.10 g/cm^3. It is probable that various microdefects, micropores, microcracks, segregations, and other discontinuities in the electronic density arise in the course of sample preparation (compression, sintering of the components, and firing).

To determine the size of such discontinuities, small angle x-ray scattering of the samples was determined in a KRM-1 small-angle camera in filtered copper radiation within the angle range from 10 to 120′. Samples for small angle scattering

TABLE 2

Raw material	Content, %, in mixture					
	1	2	3	4	5	6
Veselovskoe clay	10.00	10.00	10.00	12.00	11.00	17.20
Prosyanovskoe kaolin	40.00	40.00	40.00	39.00	41.80	33.70
Hälleflinta	–	–	–	49.00	–	–
Pegmatite	32.00	34.00	29.74	–	–	–
Nepheline-sienite	–	–	–	–	–	25.00
Quartz porphyry	–	–	–	–	33.90	–
Quartz	18.00	16.00	20.26	–	10.80	19.00
Porcelain scrap after firing	–	–	–	–	–	5.00
Alumina	–	–	–	–	2.50	–

which were less than 0.4 mm thick were prepared on a grinding wheel.

Figure 1 shows the relationship between the small-angle scattering intensity and the angle $I(\varepsilon)$ for samples of mixtures 1, 2, 4, and 6. The biggest differences in the pycnometric density are observed in mixtures 1 and 4. The radii of electronic density discontinuities were calculated by the tangent method [3]. The algorithm of calculation has been developed for MathCAD software.

The dependence $I(\varepsilon)$ rapidly drops as the scattering angle increases. This indicates the existence of micripores of the same size in samples 1, 2, and 6. It has been theoretically established that the size of the micropores in samples 1, 2, and 6 differs from 230 to 320 Å. Sample 4 contains microholes having a maximum size of 600 Å and a minimum size of 180 Å. The scattering intensity of sample 4 for the smallest registered scattering angle are 2 times higher than those of samples 1, 2, and 6. The main effect on the porosity of sample 4 is determined by the minimum-sized (radius from 10 ± 5 to 50 ± 5 Å) pores: 3.1%, medium-sized pores — 2.3%, large pores — 0.1%.

The microstructure of experimental porcelain mixtures 1 and 4 (Fig. 2) supports the results of the small angle x-ray scattering analysis. The microstructure of mixture 1 (based on plagioclase pegmatite) after firing at temperature of 1250 – 1320°C exhibits undissolved feldspar and quartz grains. Figure 2*b* shows mixture 4 with the hälleflinta concentrate. Its microstructure within the sintering temperature interval of 1250 – 1320°C is distinguished by the microporosity of the vitreous phase, and feldspar and quartz grains are absent.

The petrographic study results agree with the x-ray analysis: the porcelain sample structure is represented by a brownish-gray vitreous substance with mullite and quartz crystals. Fragments of quartz grains 0.09 – 0.04 mm in size of different shapes are typical of the mixture 4 sample. Segments of an edge (0.001 mm and smaller) are seen along certain grains. Larger grains of quartz (0.16 – 0.12) are preserved in sample 1.

Two types of pores are seen in the vitreous matrix of sample 4: small rounded isolated pores 0.01 mm in size — 1 – 2%, and larger isometric pores 0.04 – 0.06 and 0.08 – 012 mm in size — 1.5%. The boundaries of single grains of crushed feldspar are distinguishable in samples 1 and 5.

Thus, it can be inferred that feldspar concentrates based on rocks of different genetic types, with different contents of microcline, albite, anorthite, and quartz, do not affect the phase composition but affect the formation temperature interval and the structure (porosity) of the vitreous phase of the porcelain mixtures. The fine-grained structure of quartz and the eutectic ratio of quartz and albite in hälleflinta intensify the process of the vitreous phase formation in the porcelain mixture.

It is known that the properties of ceramics largely depend on the properties arising in firing of the crystal and vitreous phases. The considered mixtures in firing form vitreous phases of different compositions depending on the potassium and sodium oxide content in the feldspar concentrates. The quantitative content of the vitreous phase in the mixtures is substantial; therefore its properties to a great extent determine the properties of the product [2].

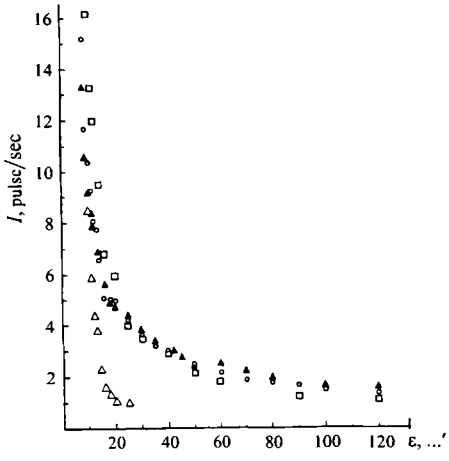

Fig. 1. Angle dependences of scattering intensity: △) mixture 4; □) mixture 1; ○) mixture 2; ▲) mixture 6.

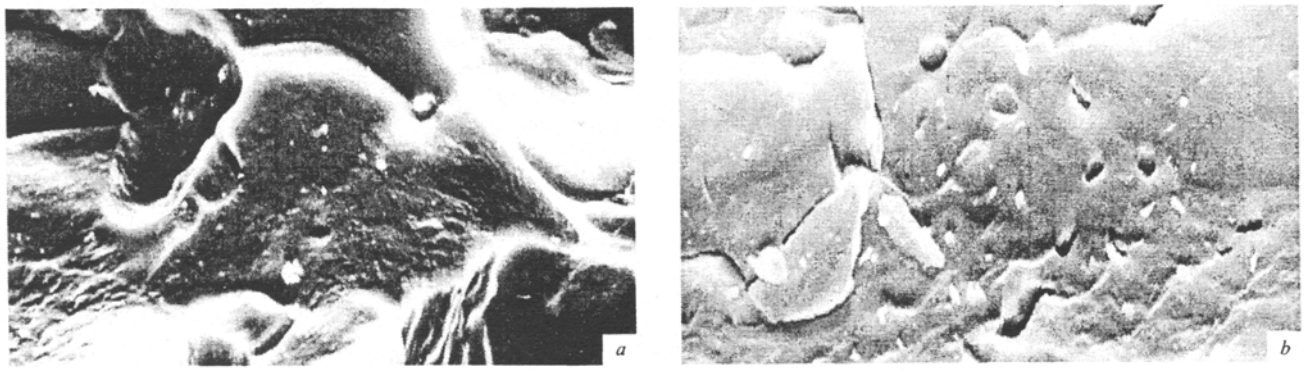

Fig. 2. Microstructure of porcelain mixtures 1 (*a*) and 4 (*b*).

TABLE 3

Parameter*	Sample of mixture					
	1	2	3	4	5	6
Mixture moisture in molding, %	24.2	23.9	24.0	24.7	24.4	24.1
Linear shrinkage after drying at 110°C, %	4.2	4.0	3.6	3.7	4.2	3.7
Linear shrinkage, %, after firing at:						
950°C	3.8	3.7	3.9	3.8	4.4	3.8
1280°C	10.8	12.9	11.3	11.4	11.2	10.1
1320°C	12.7	13.1	12.3	11.7	10.3	12.7
1380°C	12.1	12.8	11.8	11.5	10.8	12.5
Water absorption, %, after firing at:						
950°C	15.80	16.00	16.20	15.00	18.00	18.30
1280°C	0.11	0.18	0.17	0.17	0.21	0.29
1320°C	0.09	0.05	0.06	0.01	0.10	0.11
1380°C	0.05	0.08	0.09	0.06	0.03	0.07
Bending strength, MPa, after firing at:						
950°C	55.7	56.6	58.9	67.4	63.0	45.3
1280°C	68.9	70.7	69.1	73.9	72.8	76.2
1320°C	71.3	78.2	79.2	83.6	81.9	79.7
1380°C	69.4	75.3	76.5	81.4	79.5	78.3
Whiteness, %, after firing at:						
1320°C	69.1	67.5	67.1	75.5	61.1	68.5
1380°C	65.3	63.8	63.9	69.7	60.3	65.2

* Heat resistance of all samples was 12 thermal cycles.

The properties of the experimental mixture are shown in Table 3. It can be seen that based on the parameters of shrinkage, porosity, and water absorption, the sintering interval of the experimental porcelain mixtures varies within the interval of 1250 – 1320°C for mixtures 2, 3, and 4 and within the range of 1280 – 1380°C for mixtures 1, 5, and 6. The bending strength increases as the firing temperature increases. The high bending strength index in sample 4 based on the hälleflinta quartz-feldspar concentrate suggests that its strength increases as a consequence of intense dissolution of finely disperse quartz in sodium glass. The vitreous phase structure in this case is more homogeneous, with uniform distribution of the minimum-size pores of the radius between 10 and 50 Å over the entire body, which also contributes to light scattering and improves the sample whiteness up to 75.5%.

Thus, feldspar concentrates based on Karelian mountain rocks differ in their chemical and mineralogical compositions and in size of quartz and feldspar grains, which significantly affects their concentration capacity.

Not only the chemical and mineralogical composition, but the grain structure and the ratio of quartz and feldspar in the feldspar concentrate, are of considerable importance for the formation of the vitreous phase in ceramic samples firing.

The eutectic ratio of quartz and albite in hälleflinta intensifies the formation of the vitreous phase at low firing temperatures. The fine-grained structure of hälleflinta contributes to the formation of the minimum-size micropores with the radius ranging from 10 ± 5 to 50 ± 5 Å. The concentration of quartz in the vitreous phase as a consequence of dissolution of finely disperse quartz in sodium glass improves the service qualities of the porcelain. By the combination of the physicotechnical parameters, the mixture based on hälleflinta differs from the mixtures based on the concentrates of other plagioclase rocks (pegmatites, alkaline sienites) in that the vitreous phase in the mixture based on hälleflinta is formed at a lower temperature (1250 – 1350°C) than in the mixture based on pegmatite (1280 – 1380°C). The mixture with hälleflinta has high mechanical strength (83.6 MPa) and whiteness (75.5%).

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